GaN:Eu Interrupted Growth Epitaxy (IGE): Thin Film Growth and Electroluminescent Devices

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ABSTRACT

The GaN:RE phosphor development plays a major role in the GaN:RE AC thick dielectric electroluminescent (TDEL) device optimization. In this paper we report on EL devices fabricated using Eu-doped GaN red phosphors films grown by *interrupted growth epitaxy (IGE)*. IGE consists of a sequence of *ON/OFF* cycles of the Ga and Eu beams, while the N_2 plasma is kept constant during the entire growth time. IGE growth of GaN:Eu resulted in significant enhancement in the Eu emission intensity based primarily at 620.5nm. The increase in the material crystallinity observed with the IGE phosphors appears to be the dominant cause of the emission enhancement. Thick dielectric EL devices fabricated on glass substrates using IGE-grown GaN:Eu have resulted in luminance of ~1000 cd/m^2.

INTRODUCTION

During GaN:RE growth RE ions compete for the substitutional vacancies in the Ga sub-lattice. Therefore, slightly nitrogen-rich growth conditions are more suitable for RE incorporation. Nevertheless, the deviation from the stoichiometric growth condition adversely affects the crystallinity of the material. Poor crystallinity in the phosphor material hinders the hot carrier transport quality and therefore the electroluminescence (EL).

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In conventional MBE, all molecular beams (Ga and N) are incident upon the growth surface simultaneously throughout the entire period and the constituent atoms and molecules are deposited on the substrate preferably under stable group V conditions resulting a continuous growth. The short nitrogen radical lifetime on the surface allows only for very rapid reaction of Ga and N and immediate formation of GaN crystals [1]. Therefore, the MBE growth technique frequently results in the formation of a large number of GaN islands on the substrate surface due to the severe limitations in Ga atom migration on the surface at the relatively low MBE growth temperatures [2, 3]. The island formation tends to induce a columnar growth of the material and results in poor morphology and electrical properties.

Several techniques have been investigated in order to enhance the quality of the semiconductor material, including shutter control method [4], nitrogen beam modulation [5], and migration enhanced epitaxy (MEE) [6]. All these techniques have as a common feature the goal of increasing the surface migration of Ga atoms during GaN growth. A schematic illustrating the source shutter sequences in MBE and MEE processes is shown in Fig. 1. The nitrogen flux is interrupted periodically at a constant Ga flux to facilitate the surface migration of the Ga atoms. In MEE, the nitrogen and Ga shutters are modulated consecutively with no overlap for periods in the order of seconds (~1-2 seconds [7] and 20-40 seconds [4]). MEE growth improvements are less pronounced at higher growth temperatures, where the Ga atoms have higher surface mobility. Horikoshi [8] provides an excellent review of the MEE growth technique.
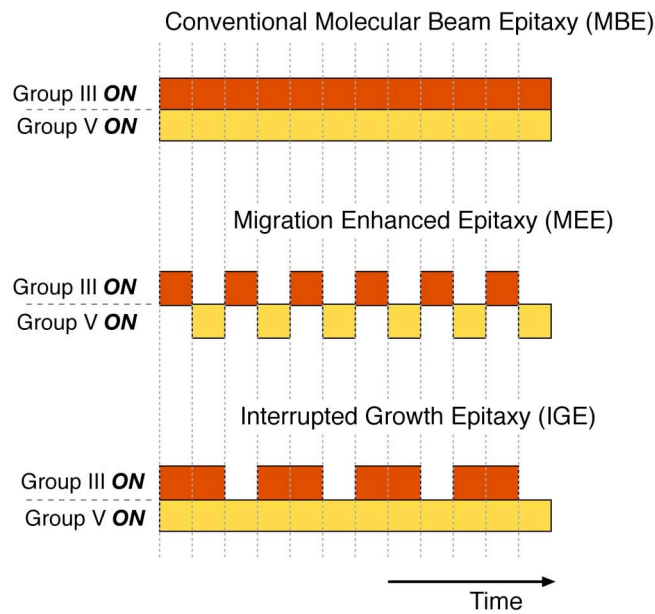

Fig. 1   Illustration of the shutter sequences in GaN:RE MBE, MEE and IGE growth techniques.

The novel growth technique discussed here, named *interrupted growth epitaxy* (IGE), is a modification of conventional molecular beam epitaxy (MBE) where the group III beams (Ga, Al, RE^{3+}) are cycled *ON* and *OFF* while maintaining a constant group V beam (N) (Fig. 1). In contrast to MEE, in IGE relatively long periods (from a few minutes to tens of minutes) of growth are used where all beams are incident on the substrate followed by periods where only selected beams are incident. Using IGE EL phosphor material of higher quality can be synthesized compared to conventional MBE while employing the same growth conditions (beam pressure, substrate temperature, etc.) as conventional MBE.

EXPERIMENTAL PROCEDURE

The different group III cycling sequences employed to evaluate the IGE technique in the preliminary study are shown in Table 1. The second and third columns in the table 1 show the duration for which the group III (Ga and Eu) shutters are open and closed during a cycle, respectively. Column four in table 1 shows the time the group V shutter is open during a single cycle (this corresponds to the total cycle time). The sequence with a 60min group III cycling time has both group III and V continuously flowing for the entire duration, in other words conventional MBE growth (i.e. all shutters simultaneously open). All other growth sequences utilized a 5 min group III *OFF* time (i.e. only group V is on) introduced between consecutive group III *ON* cycles. The total group III *ON* time for all sequences is kept constant at 60 minutes.

GaN:Eu Sample No.	Shutter open/closed time during one cycle			No. of cycle repetitions
	Group III *ON*	Group III *OFF*	Group V *ON*	
C089	60 min	0 min	60 min	1
C093	30 min	5 min	35 min	2
C095	20 min	5 min	25 min	3
C094	15 min	5 min	20 min	4
C091	10 min	5 min	15 min	6
C090	5 min	5 min	10 min	12

Table 1   The different group III cycling sequences employed to evaluate the IGE technique in the preliminary study in GaN:Eu phosphor growth.

We assumed that the growth of material occurs only during the time period when both group III and V shutters were open and that the loss of material through disassociation during the group III *OFF* period is essentially negligible when designing these growth sequences. Achieving a 0.7µm/hr growth rate for all the films validated this assumption. MBE growth parameters were Ga cell at 900 °C with a beam equivalent pressure (BEP) of ~4.1x10^{-7} torr and Eu cell at 440 °C. The Eu incorporation in the films was found to be ~0.1 at.%, which is below the onset of luminescence concentration quenching. The growth was carried out at 650°C for Si substrates. Growth was at 800°C thermocouple temperature on glass substrates and ceramic back plates were used for maximum heat transfer. The RF nitrogen plasma was set at a gas flow of 1.8 sccm with 400W forward power to achieve the optimum growth condition.

RESULTS AND DISCUSSION

Material Characterization

To understand the IGE growth technique a controlled experiment was carried out on undoped GaN. The material growth was conducted in both conventional MBE and IGE techniques. Other than the dissimilarity in growth technique all other growth parameters were kept constant. It is important to point out that the growth parameters were not optimized to yield the best GaN epi-layers: slightly Ga-rich conditions are preferred for high quality GaN growth and slightly N-rich conditions are preferred for GaN:RE phosphor growth. Since the objective of these experiments was to understand the IGE effect on GaN:Eu material growth for photonic applications, a III/V ratio that is slightly N-rich (optimized for GaN:Eu growth) was used.

Obviously, the best material crystalline quality is desired in GaN:RE phosphor material for efficient ACTDEL device applications. As explained previously, the higher the crystallinity of the film the higher the probability for loss-free hot electron transport. An advantageous measurement in evaluating the film crystalline quality at different stages of growth is the *in-situ* Reflection High Energy Electron Diffraction (RHEED).

Fig. 2 shows the diffraction patterns observed at 15min intervals for a conventional MBE (Fig. 2a) and 15min IGE (Fig. 2b) growth of GaN. The polycrystalline GaN produces a spotty RHEED pattern. As the crystalline quality decays the hexagonal spotty pattern converts toward a ring shaped diffraction pattern, as seen in the conventional MBE GaN. Alternatively, when the crystallinity of the film improves, as observed with increasing number of cycles in the IGE GaN, the hexagonal spotty pattern evolves into a

streaky diffraction pattern. The fact that the 15min IGE GaN RHEED measurements show a more defined streaky pattern as the growth time progresses leads to the conclusion that the IGE technique yields better crystalline material than conventional MBE at process parameters optimized for GaN:RE phosphor growth.
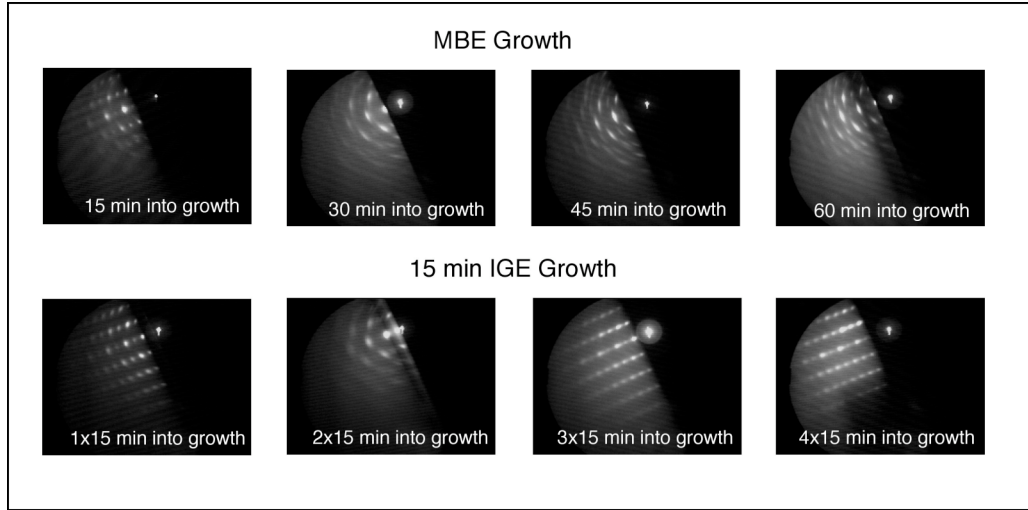

Fig. 2   RHEED patterns observed for *un-doped* GaN epi layers using conventional MBE growth and 4×15 min IGE growth. Except for the growth cycling conditions all other growth parameters are identical on both growths.
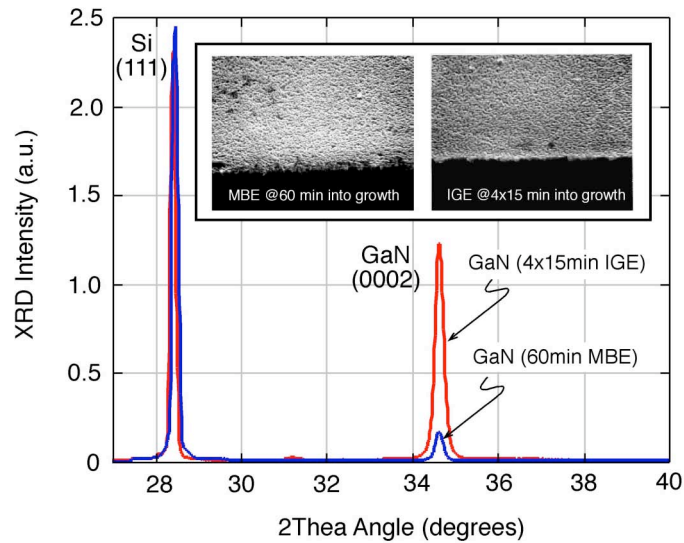

Fig. 3   XRD spectra for *un-doped* GaN epi layers using conventional MBE growth and 4×15 min IGE growth. SEM microphotographs of *un-doped* GaN epi layers using conventional MBE growth and 4×15 min IGE growth are shown in the inserts.

The basic material characterization techniques used for characterization of the undoped GaN IGE epi layers are scanning electron microscopy (SEM) and x-ray diffraction (XRD). Fig. 3 illustrates the XRD spectra for the 4×15 min IGE and 60 min MBE GaN samples. The inserts of Fig. 3 show SEM microphotographs of both films. It is clear from the high intensity of the GaN (0002) peak at 34.5° in the IGE GaN film that IGE produces films with a higher crystalline quality compared to conventional MBE. The peak observed at 28.4° is the (111) peak from the Si substrate. The above characterization methods have proven that GaN epi layers with relatively high crystalline quality can be grown under slightly N-rich conditions utilizing the interrupted growth epitaxy technique than with the conventional MBE.

Initial studies on the IGE growth effects on GaN:RE was carried out through GaN:Eu grown on (111) Si substrates. After growth, the first evaluation of material quality as an electroluminescent phosphor is photoluminescence (PL). The PL characterization at Cincinnati is carried out at room temperature using UV (325nm) photons from a He-Cd laser. First, the UV photons are absorbed in the GaN host, generating electron-hole pairs. Subsequently, the energy of the photo-generated carriers is transferred to Eu centers in the GaN host, causing their transition to an excited state from which they can relax by the emission of photons of well defined energies [9, 10, 11].
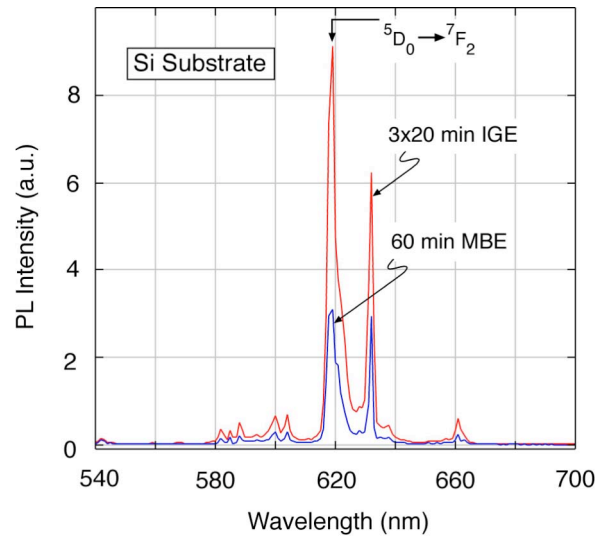
Fig. 4   Photoluminescence spectra of GaN:Eu samples grown using various 3×20 min IGE and 60 min MBE on Si substrates. Above bandgap PL was measured at room temperature under 325nm HeCd laser excitation.

Fig. 4 illustrates above bandgap PL spectra for GaN:Eu films grown by 3×20 min IGE and 60 min MBE. No GaN band edge emission (at ~365nm) is observed for either film. Efficient transfer of energy from the

host to the Eu ions followed by radiative relaxation and reduced crystallinity in the GaN layer due to Eu doping and the relatively low temperature growth may have caused the absence of GaN band edge emission. The most prominent emission peaks in the spectrum at red wavelengths are at 621nm and 632nm, which correspond to the Eu intra-4f transitions ${}^5D_0{\rightarrow}{}^7F_2$ and ${}^5D_1{\rightarrow}{}^7F_4$ (tentatively assigned), respectively. Clearly the IGE growth technique has a strong influence on the Eu emission intensity. Comparing, the intensity of the ${}^5D_0{\rightarrow}{}^7F_2$ transition from the IGE sample to the MBE sample, we can see that the former has ~3× higher peak intensity. There are several possible explanations for this effect: (a) improvements in crystallinity of IGE films; (b) location of Eu^{3+} ions at different site environments during IGE vs. MBE growth. The increase in the PL intensity also indicates that the IGE technique results in more optically active Eu^{3+} ions than the conventional MBE technique.
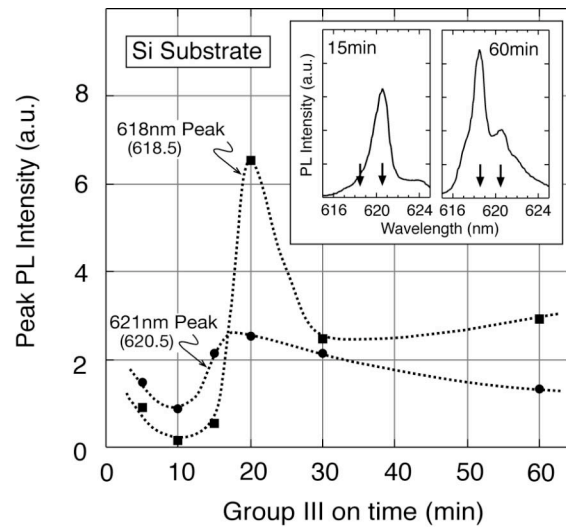

Fig. 5   Peak PL intensity at 621nm and 618nm against various IGE *ON* times on Si substrates. Inserts show the PL spectra from GaN:Eu samples with 15min and 30 min IGE *ON* times.

Careful examination of the PL spectra for different IGE GaN:Eu films show an interesting transition in the intensity of the major red emission peak at different group III *ON* times. Fig. 5 shows the variation of the 618 and 621nm peak intensities with IGE conditions. The accurate wavelengths for the peaks that we refer to as 618 and 621nm are 618.5 and 620.5nm, respectively. As also shown in the Fig. 5 inserts, at shorter IGE *ON* times (<15min) the major Eu red emission is at 621nm, whereas for longer (>20min) IGE *ON* times the 618nm peak is dominant. This shift of the dominant Eu emission from the 621nm peak to the 618nm peak with the increase in IGE cycling time can be attributed to changes in Eu incorporation

(different concentration of various sites) in the host material structure due to the growth condition variations.

Further insight into the emission characteristics of IGE GaN:Eu has been reported by Hömmerich et *al.* [12] through a combination of above-bandgap (333-363nm) and resonant (477nm) excitation. Lifetime measurement using time-resolved PL has shown the existence of multiple Eu^{3+} sites within the host.

Dierolf et *al.* [13] using combined excitation emission spectroscopy have identified several defect sites in the single $^4D_0 \rightarrow {}^4F_0$ transition (Fig. 6). While the major defect sites prevail, the relative strength of the minor defects sites is strongly dependent on the preparation conditions.
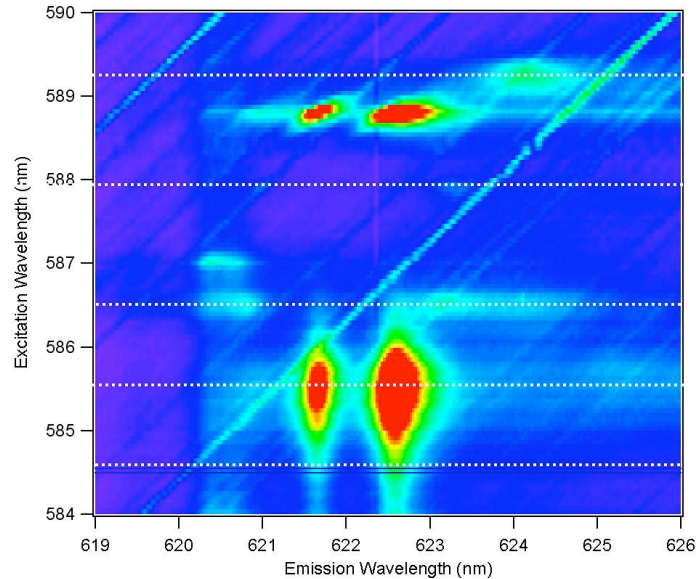

Fig. 6   Contour plot of combined excitation emission spectroscopy data for 3×20 min IGE GaN:Eu showing 5 different defect site indicated by dotted lines.

Everitt et *al.* [14] have conducted fine structure spectroscopy, time-resolved photoluminescence and photoluminescence excitation (PLE) measurements to study the energy levels and carrier relaxation dynamics of the red luminescence ($^5D_0 \rightarrow {}^7F_2$) from GaN:Eu as a function of pump energy and pump intensities. These measurements have further realized the existence of multiple Eu3+ sites within the IGE GaN:Eu.

Electroluminescent Device Characterization

The thick dielectric electroluminescent devices (TDEL) using GaN:RE phosphor material are fabricated on glass substrates [15]. A cross sectional view of the GaN:RE TDEL device is shown in the insert of Fig. 7a. The IGE GaN:Eu phosphor is encapsulated within thin barium titanate (BTO) dielectric layers for enhanced charge trapping at phosphor-dielectric interface. A high density, nano-porous PZT thick dielectric layer is incorporated to achieve high charge sourcing into the phosphor while enabling the device to endure localized imperfections (pinholes, etc.). Front and rear electrodes are used for providing the electric field. The front electrode is generally transparent for visible emission since the light emitted from the phosphor will reach the viewer through the front electrode and glass substrate.
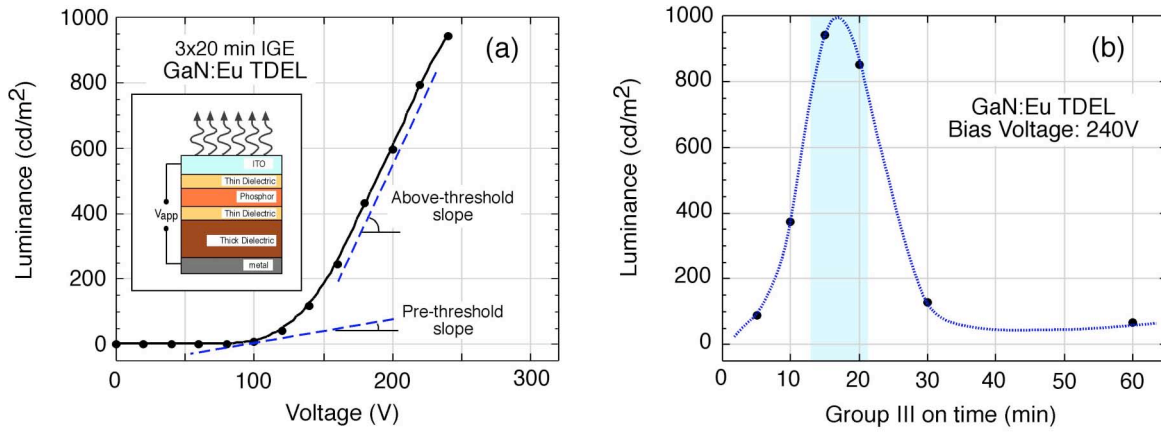

Fig. 7   (a) Luminance-voltage measurements for 3×20 min IGE GaN:Eu TDEL device. Insert shows a cross sectional view of the TDEL device. (b) luminance variation with different IGE group III *ON* times in GaN:Eu TDEL devices.

Fig. 7a presents the luminance of 3×20 min IGE GaN:Eu TDEL device as a function of voltage. The devices were driven using a 1kHz bipolar square waveform. The above-threshold and pre-threshold slope of the luminance-voltage (L-V) plot are also illustrated in Fig. 7a. Clearly, for the best device performance the highest above-threshold slope and lowest pre-threshold slope is desired. Ideally, at pre-threshold voltages the phosphor layer acts as a capacitor. In reality, however, the phosphor material always experiences some charge leakage at pre-threshold voltages. The presence of leakage charge can cause observable luminance at voltages below turn-on and results in a rather shallow rise in the luminance at modulation voltages above turn-on. Fig. 7b shows the luminance of GaN:Eu TDEL devices with varying IGE cycles. The luminance is measured at a 240V bias at 1kHz. The strongest device luminance

of nearly ~1,000 cd/m^2 is observed for GaN:Eu layers with 3×20 min IGE, representing a >10× increase over devices fabricated using 60 min MBE GaN:Eu.
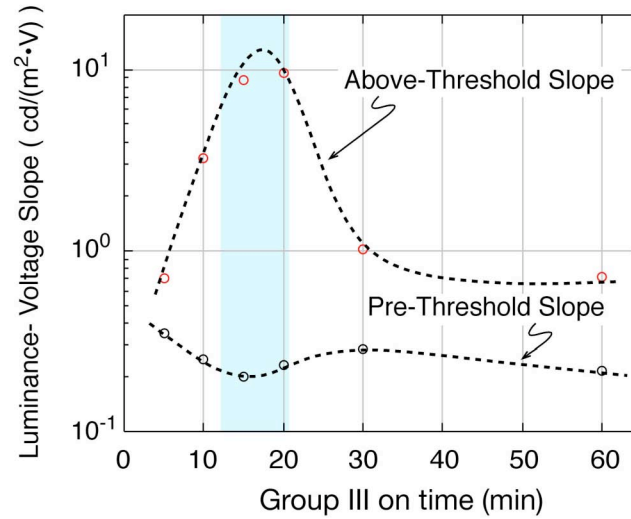

Fig. 8   Device luminance-voltage slope measured at pre-threshold and above-threshold luminance for IGE GaN:Eu TDEL devices using films grown with different group III *ON* times. The TDEL devices were driven using bipolar square waveform at 1kHz.

The above threshold luminance-voltage slope illustrated in Fig. 8 for the optimum IGE devices is much steeper than in the MBE device. In addition, the pre-threshold luminance-voltage slope for the optimal IGE devices is at the minimum when compared with the MBE device. The sharper luminance increase with increasing voltage is due to the increase in luminance efficiency. A possible reason for increased device efficiency in the IGE process is the improvement made in the hot electron transport of GaN:Eu [16].The pre-threshold luminance reduces the high contrast that is desired in flat panel displays. The 3×20 min IGE GaN:Eu TDEL device displays a ~10× improvement in contrast over the conventional 60 min MBE GaN:Eu devices.

CONCLUSIONS

In conclusion, the IGE technique has demonstrated a significant step forward in optimization of GaN:RE thin films and EL devices. Devices grown with 3×20 min IGE cycles have produced a >10× improvement in EL luminance over conventional MBE phosphors, reaching ~1,000 cd/m^2. The PL measurements of IGE films and devices with various group III cycling indicate the possibility of situating Eu atoms in at

least two distinct sites within the GaN host. It appears that, the site location of the Eu lumophore could be controlled through varying the IGE growth parameters systematically. Furthermore, the IGE growth technique has proven itself as an effective method of increasing the excitable lumophore concentration in EL devices.

ACKNOWLEDGEMENTS

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